

## METHOD OF RECOVERING HYDROCHLORIC ACID

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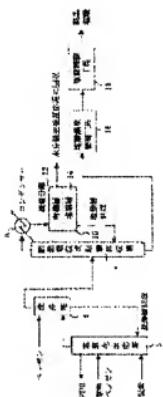
Priority number(s): JP20000074213 20000316

Abstract of IP 2001261308 (A)

**PROBLEM TO BE SOLVED:** To provide a method of recovering hydrochloric acid by which the content of organic compounds in hydrochloric acid formed as a by-product in chlorinating reaction of an aromatic hydrocarbon such as benzene is reduced. **SOLUTION:** A reaction gas containing chlorine and hydrogen chloride gas produced in a chlorinating reaction is brought into contact with benzene in a recovering column 4 to absorb and remove organic compounds having a higher boiling point than that of benzene and contained in the reactional gas in the benzene.; The reactional gas after the absorption and removal is then fed to an adsorption type hydrochloric acid recovering column 6 to obtain crude hydrochloric acid from the column bottom of the recovering column 6 and a discharged gas is obtained from the column top of the recovering column 6 when the benzene is chlorinated in a chlorinating reactional column 2 to produce p-dichlorobenzene.

**Also published as:**

JP4389327 (B2)



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LI ANSWER 4 OF 5 HCAPLUS COPYRIGHT 2010 ACS on STN  
AN 2001:707116 HCAPLUS [Full-text](#)  
DN 135:259313  
TI Recovery of hydrochloric acid in manufacture of chlorinated aromatic hydrocarbons.  
IN Sato, Akio; Katsuo, Chizu  
PA Toa Gosei Chemical Industry Co., Ltd., Japan  
SO Jpn. Kokai Tokkyo Koho, 6 pp.  
CODEN: JKXXAF  
DT Patent  
LA Japanese  
FAN.CNT 1

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PI JP 2001261308 20000316 <-- PRAI JP 4389327 JP 2000-74213	A B2 20091224 20000316	20010926	JP 2000-74213	

AB In manufacture of chlorinated aromatic hydrocarbon by chlorination of aromatic hydrocarbon (e.g., benzene), chlorination generated HCl-containing reaction gas is introduced into a cleaning column for contacting with raw material aromatic hydrocarbon for removing reaction gas-contained organic compds. having higher b.p. than that of the aromatic hydrocarbon by absorption, and then sending the above stated organic compds.-removed reaction gas to an adiabatic absorption-type HCl recovery column for obtaining crude hydrochloric acid from the bottom of the column, and discharging waste gas from the top of the column.

L3 ANSWER 4 OF 5 WPIX COPYRIGHT 2010 THOMSON REUTERS on STN  
AN 2002-125724 [200217] WPIX Full-text  
DNC C2002-038844 [200217]  
TI Hydrochloric acid recovery from reactive by-product gas of aromatic  
hydrocarbon chlorination, involves contacting reactive gas with aromatic  
hydrocarbon and passing to heat insulation absorption type recovery tower  
DC E19; E36; J01  
IN KATSUO C; SATO A  
PA (TOAG-C) TOA GOSEI CHEM IND LTD  
CYC 1  
PI JP 2001261308 A 20010926 (200217)\* JA 6[1]  
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JP 4389327 B2 20091224 (201001) JA 9  
ADT JP 2001261308 A JP 2000-74213 20000316; JP 4389327 B2 JP  
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FDT JP 4389327 B2 Previous Publ JP 2001261308 A  
PRAI JP 2000-74213 20000316  
IPCI C01B007-00 [I,C]; C01B007-01 [I,A]; C07C0017-00 [I,C]; C07C0017-06  
[I,A]; C07C0017-38 [I,A]; C07C0025-00 [I,C]; C07C0025-08 [I,A]  
IPCR B01D0053-14 [I,A]; B01D0053-14 [I,C]; C01B0007-00 [I,C]; C01B0007-01  
[I,A]; C07B0061-00 [I,A]; C07B0061-00 [I,C]; C07B0063-00 [I,A];  
C07B0063-00 [I,C]; C07C0017-00 [I,C]; C07C0017-06 [I,A]; C07C0017-38  
[I,A]; C07C0025-00 [I,C]; C07C0025-08 [I,A]  
FCL B01D0053-14 103; B01D0053-14 C; C01B0007-01 J; C07B0061-00 300;  
C07B0063-00 B; C07B0063-00 G; C07C0017-06; C07C0017-38; C07C0025-08  
Main: C01B0007-01 J  
Secondary: B01D0053-14 103; B01D0053-14 C; C07C0017-06; C07C0017-38;  
C07C0025-08  
Additional: C07B0061-00 300; C07B0063-00 B; C07B0063-00 G  
FTRM 4D020; 4G041; 4H006; 4H039; 4H006/AA02; 4H006/AA04; 4D020/AA10;  
4H006/AC30; 4H006/AD16; 4H006/AD18; 4H006/BA09; 4D020/BA15;  
4H006/BA19;  
4H006/BA39; 4H006/BA68; 4H006/BA71; 4D020/BB04; 4D020/BC01;  
4D020/BC10;  
4H006/BC52; 4H006/BD82; 4H006/BD84; 4H006/BE53; 4H039/CA52;  
4D020/CB01;  
4D020/CB08; 4D020/CB18; 4D020/CB25; 4D020/CB28; 4D020/CD10;  
4H039/CD20;  
4H006/EA21  
AB JP 2001261308 A UPAB: 20050524  
NOVELTY - Reactive gas obtained during chlorination of aromatic hydrocarbon (ARH) and containing hydrogen chloride and chlorinated ARH is contacted with the ARH. High boiling chlorinated ARH are removed by absorption and reactive gas is sent to heat insulation absorption type hydrochloric acid recovery tower (6). Crude hydrochloric acid is obtained from the tower bottom and exhaust gas is extracted from the tower top.

USE - For recovery of hydrochloric acid from hydrogen chloride reactive gas formed as a by-product in the chlorination of aromatic hydrocarbons e.g. benzene, toluene.

ADVANTAGE - Large amount of hydrogen chloride gas is generated. Substitution of high boiling chlorinated aromatic hydrocarbon with low boiling aromatic hydrocarbon prevents condensation of organic compound in the recovery tower. Organic compound content in the crude hydrochloric acid is reduced. Liquid separation is performed efficiently since the amount of chlorinated aromatic hydrocarbon is less and specific gravity of the organic layer is small. Separation results in high purity organic layer and salt acid layer thereby enabling effective recycle of pure hydrochloric acid.

DESCRIPTION OF DRAWINGS - The figure shows the flow chart of the manufacturing apparatus used for recovering hydrochloric acid. (The drawing includes non-English language text)

Chlorination reaction tower (2)  
Scrubbing tower (4)  
Heat insulation absorbing type hydrochloric acid recovery tower (6)  
Liquid separator (10)  
Organic layer (12)  
Salt acid layer (14)

MC CPI: E10-H03C1; E11-Q01; E31-B02; J01-E02B

## PATENT ABSTRACTS OF JAPAN

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C07C 17/06

C07C 17/38

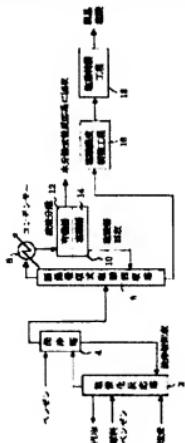
11-6078-61 (00)

607B 63/00

(21)Application number : 2000-074213 (71)Applicant : TOAGOSEI CO LTD

(22) Date of filing : 16.03.2000 (72) Inventor : SATO AKIO  
KATSUO CHIZU

(54) METHOD OF RECOVERING HYDROCHLORIC ACID



(57) Abstract:

**PROBLEM TO BE SOLVED:** To provide a method of recovering hydrochloric acid by which the content of organic compounds in hydrochloric acid formed as a by-product in a chlorinating reaction of an aromatic hydrocarbon such as benzene is reduced.

**SOLUTION:** A reactional gas containing hydrogen chloride gas produced in a chlorinating reaction is brought into contact with benzene in a washing column 4 to absorb and remove organic compounds having a higher boiling point than that of benzene and contained in the reactional gas in the benzene. The reactional gas after the absorption and removal is then fed to an adiabatic absorption type hydrochloric acid recovering column 6 to obtain crude hydrochloric acid from the column bottom of the recovering column 6 and a discharged gas is obtained from the column top of the recovering column 6 when the benzene

is chlorinated in a chlorinating reactional column 2 to produce p- dichlorobenzene.

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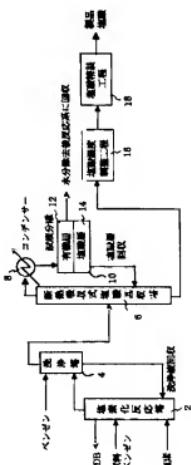
最終回に詠べ

(54) [透明の多様] 旗臈の回収方法

(57)【要約】

【課題】ベンゼン等の芳香族炭化水素の塩素化反応において副生する塩酸中の有機化合物含有量を低減させる塩酸の回収方法を提供する。

【解決手段】 ベンゼンを塩素化反応塔2で塩素化してp-ジクロロベンゼンを製造するに当り、前記塩素化反応において発生する塩化水素ガスを含む反応ガスを洗浄塔4でベンゼンと接触させて前記反応ガス中に含まれるベンゼンよりも高沸点の有機化合物をベンゼンに吸収除去させ、次いで吸収除去後の反応ガスを断熱吸収式塩素回収塔6に送り、回収塔6の塔底から粗塩酸を得ると共に、回収塔6の塔頭から排出ガスを得る。



## 【特許請求の範囲】

【請求項1】 芳香族炭化水素の塩素化反応により塩素化芳香族炭化水素を製造するに当たり、前記塩素化反応において発生する塩化水素ガスを含む反応ガスを原料の芳香族炭化水素と接触させて前記反応ガス中に含まれる該芳香族炭化水素よりも高沸点の塩素化芳香族炭化水素を該芳香族炭化水素に吸収除去させ、次いで吸収除去後の反応ガスを断然吸収式塩酸回収塔に送り、塔底から粗塩酸を得ると共に、塔頂から排出ガスを抜出すことを特徴とする塩酸の回収方法。

【請求項2】 排出ガスを凝縮させ、原料の芳香族炭化水素を主成分とする有機層と塩酸層とに液液分離し、前記有機層を脱水後、塩素化反応に再利用する請求項1に記載の塩酸の回収方法。

【請求項3】 排出ガスを凝縮させ、原料の芳香族炭化水素を主成分とする有機層と塩酸層とに液液分離し、前記塩酸層を断然吸収式塩酸回収塔に送る請求項1に記載の塩酸の回収方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明はベンゼン、トルエン等の芳香族炭化水素の塩素化反応において副生する塩化水素ガスから塩酸を回収する方法に関する。

## 【0002】

【従来の技術】 ベンゼンを塩素化して得られるジクロロベンゼン(DCB)は工業的に重要な化合物である。ジクロロベンゼンには、オルトジクロロベンゼン(o-DCB)、メタジクロロベンゼン(m-DCB)、パラジクロロベンゼン(p-DCB)の3異性体がある。これら3異性体の内、PDCBは最も需要が多く、防虫剤等に利用され、またエンジニアリングプラスチックであるポリフェニレンサルファイドの原料として注目されている。

【0003】 従来、ジクロロベンゼンは、塩化第二鉄等のフリーデルクラフト型触媒を用いてベンゼン(BZ)またはクロロベンゼン(CB)を塩素化することにより製造されている。

【0004】 製造時にパラジクロロベンゼンの選択率を高めるため、硫黄、セレン系の無機または有機化合物と塩化第二鉄とを触媒として併用する方法も提案されている。

【0005】 更に、ゼオライトを触媒として用いることにより、ベンゼンまたはモノクロロベンゼンの塩素化反応において、パラジクロロベンゼンの選択率を高める技術も提案されている(特開昭57-777631号公報、特開昭59-163329号公報)。

また更に、触媒として活性アルミナを使用することにより從来技術の有する活性を解決する技術も開示されている(特開平1-93550号公報)。

## 【0006】 これらの製造方法においては、何れもベン

ゼンは気相または液相中で触媒の存在下に塩素化されるが、この塩素化反応においては、塩化水素が副生され、これが副生塩化水素ガスとして外部に取出される。前記外部に取出される副生塩化水素ガス中には、塩素化反応の原料であるベンゼン、及び反応生成物であるクロロベンゼン、ジクロロベンゼン、トリクロロベンゼン(TCB)等の各種塩素化ベンゼンが少なくともその蒸気圧に応じて含有されているので、前記副生塩化水素ガスを予め冷却してベンゼンや塩素化ベンゼンを凝縮し、回収、利用することが行われている。

【0007】 しかし、前記凝縮による回収は完全なものではなく、冷却温度におけるベンゼン等の各有機化合物の蒸気圧に相当する量は依然として副生塩化水素ガス中に残存しており、このためこの副生塩化水素ガスを塩酸回収塔に送り、ここで水と接触させて得られる塩酸中には、これらの塩素化ベンゼン等が含まれている。

【0008】 また、塩酸回収塔の塔頂側から取出される排出ガスには、水と塩化水素以外にベンゼンや塩素化ベンゼンが含まれており、これらは冷却されることにより凝縮し、ベンゼンを主成分とする有機層と塩酸層とに層分離する。通常、層分離したこれらの有機層と塩酸層とは液液分離される。しかし、前記有機層は、塩素化ベンゼンを含んでいているため比重が塩酸に近い。このため塩酸層と有機層との液液分離は困難であり、その結果その後の塩酸精製工程に支障をもたらすようになると共に、前記有機層を回収して再度製造原料として用いることも困難になる等の問題がある。

## 【0009】

【発明が解決しようとする課題】 本発明者等は、上記問題を解決するために種々検討した結果、ベンゼンの塩素化反応で発生する副生塩化水素ガスをベンゼンと接触させることにより、副生塩化水素ガス中に含有される塩素化ベンゼンをベンゼンと置換させた後、断然吸収式回収塔に送って粗塩酸を製造するようにすると、回収塔の塔底から取出される粗塩酸中の有機物含有量を大幅に減少させ得ると共に、塔頂から取出される排出ガスは、冷却することにより凝縮して塩酸層と有機層とに分離するが、有機層はベンゼンを主成分とするため比重が塩酸層よりも充分小さく、このため簡単に上記2層は液液分離でき、このようにして得られた各層はそれぞれ有効利用できることを知得した。更に、上記方法はベンゼンに限られず、各種の芳香族化合物一般に適用できることを知得した。本発明は、上記知見に基づき完成するに至つたものである。

【0010】 従って、本発明の目的とするところは、従来の問題点を解決する塩酸の回収方法を提供することにある。

## 【0011】

【課題を解決するための手段】 上記目的を達成するための本発明は以下に記載するものである。

【0012】〔1〕 芳香族炭化水素の塩素化反応により塩素化芳香族炭化水素を製造するに当り、前記塩素化反応において発生する塩化水素ガスを含む反応ガスを原料の芳香族炭化水素と接触させて前記反応ガス中に含まれる該芳香族炭化水素よりも高沸点の塩素化芳香族炭化水素を該芳香族炭化水素に吸収除去させ、次いで吸収除去後の反応ガスを断熱吸収式塩酸回収塔に送り、塔底から粗塩酸を得ると共に、塔頂から排出ガスを抜出すことを特徴とする塩酸の回収方法。

【0013】〔2〕 排出ガスを凝縮させ、原料の芳香族炭化水素を主成分とする有機層と塩酸層とに液液分離し、前記有機層を脱水後、塩素化反応に再利用する〔1〕に記載の塩酸の回収方法。

【0014】〔3〕 排出ガスを凝縮させ、原料の芳香族炭化水素を主成分とする有機層と塩酸層とに液液分離し、前記塩酸層を断熱吸収式塩酸回収塔に返送する〔1〕に記載の塩酸の回収方法。

【0015】以下、図面を参照して本発明を詳細に説明する。

#### 【0016】

【発明の実施の形態】図1は本発明の塩酸の回収方法を組込んだp-ジクロロベンゼンの製造装置の一例を示すフロー図である。

【0017】図1中、2は塩素化反応塔で、内部に触媒が充填されている。触媒としては、公知の活性アルミニウム、シリカ・アルミナ、結晶性アルミニウムシリケート等の固体酸触媒や、塩化鉄、塩化アルミニウム等のフリーデルクラフト型触媒等が例示される。前記塩素化反応塔2には、原料の芳香族炭化水素であるベンゼン及び塩素等が供給され、塩素化反応塔2内でこれらが反応して、p-ジクロロベンゼンを主成分とする塩素化ベンゼンが反応生成物として取出される。この反応自体は公知のものである。

【0018】前記塩素化反応においては、反応ガスが発生するが、この反応ガスには塩化水素ガスを主成分とし、その他の成分として、原料ベンゼン、及びモノクロロベンゼン、o-、m-、p-ジクロロベンゼン、トリクロロベンゼン等の塩素化ベンゼンが含まれている。

【0019】この反応ガスは、塩素化反応塔2の塔頂から取出され、必要により熱交換器(不図示)を通ってここで前記塩素化ベンゼンの一部を凝縮除去された後、洗浄塔4の塔底側に送られる。

【0020】前記洗浄塔4においては、塔頂側から供給される洗浄液ベンゼンが洗浄塔4内を流下しながら、塔底側から供給され洗浄塔内を上昇する反応ガスと向流状態で気液接触を繰返し、これにより反応ガス中のベンゼンよりも高沸点の有機化合物(CB、DCB、TCB、テトラクロロベンゼン、ヘキサクロロベンゼン等の塩素化ベンゼン)が流下するベンゼンによって抽出除去される。

【0021】ベンゼンよりも高沸点の有機化合物を抽出しながら洗浄塔4内を流下したベンゼン溶液(洗浄液)は、次いで塩素化反応塔2の塔底側に返送され、塩素化反応の原料として再利用される。

【0022】洗浄塔4は、充填塔、棚段塔、満れ壁塔、スプレー塔、気泡塔等の一般的なガス吸収装置として用いられている装置が利用できる。これらの内、充填塔は圧損が比較的小さく、ガス吸収効率が高いので、好みいものである。充填塔の液/ガス流量の運転条件としては、フラッディング速度以下、特にフラッディング速度の50%前後が好みしい。

【0023】塩化水素ガスの発生量が大きく、洗浄塔の塔径が大きくなる場合は、棚段塔の使用が好みしい。

【0024】スプレー塔は反応ガス中に洗浄液ベンゼンが飛沫同伴により持込まれるので、この点に注意すれば使用できる。

【0025】洗浄塔4の操作温度は、一般に低温であるほど洗浄後の反応ガス中のベンゼン含有量が少なくなるので、低温の方が好みしい。しかし、洗浄液ベンゼンの凝固点(5°C)以上で操作する必要があるので、5~30°Cが好みしく、特に7~10°Cが望ましい。

【0026】洗浄塔4の操作圧力は、高圧の方が好みしい。高圧であるほど洗浄液ベンゼンの蒸気圧が低くなり、その結果洗浄後の反応ガス中のベンゼン含有量が減少する。しかし、高圧装置は高価であるので、1 MPa以下の圧力で操作することが好みしい。また、減圧にすると、ベンゼンや塩素化ベンゼン等の有機化合物の分圧が大きくなり、その結果、洗浄後の反応ガス中のベンゼンや有機化合物の含有量が増加するので好ましくない。従って、洗浄塔の操作圧力は、常圧~1 MPaが好みい。

【0027】洗浄塔4内を上昇して、塩素化ベンゼンのほとんどすべてが除去された反応ガスは、次いで断熱吸収式塩酸回収塔6に送られ、ここで反応ガス中の塩化水素が塔内を流下する水に吸収されて粗塩酸となり、回収塔6の塔底側から取出される。

【0028】断熱吸収式塩酸回収塔6は、構造的には、前記洗浄塔4とほぼ同一構造のものである。機能的には、回収塔6内で、反応ガス中の塩化水素が水に断熱吸収され、その際に発生する大きな溶解熱に基づく温度上昇により水が蒸発させられ、また反応ガス中に含有されているベンゼンや微量に存在する塩素化ベンゼンの凝縮が妨げられる結果、それらの有機物が粗塩酸中に混入する事が避けられる。

【0029】前記断熱吸収式塩酸回収塔6の塔底側から取出される粗塩酸は、その後塩酸濃度調整工程1.6、活性炭処理等による塩酸精製工程1.8を順次通過して、製品塩酸として取出される。

【0030】一方、断熱吸収式塩酸回収塔6の塔頂側からは、排出ガスが取出される。この排出ガスは、回収塔

6内で水と反応ガスとが向流接触することにより、反応ガス中の塩化水素ガスの大部分が吸収除去されたガスで、主として、大部分を占める水蒸気及びわずかな塩化水素ガスとベンゼンガスとからなる。

【0031】前記排出ガスは、先ずコンデンサー8を通過する際に冷却されて凝縮液になり、液液分離器10に送られ、ここで有機層12と塩酸層14とに分離される。

【0032】分離された前記塩酸層は、その後断熱吸収式塩酸回収塔6の塔頂と塔底との中間部に返送される。また、分離された前記有機層12は蒸留法や、シリカゲル、モレキュラーシーブ、無水硫酸ナトリウム等の固体脱水剤等を用いて脱水処理がなされた後、塩素化反応塔2に返送され、再利用される。上記実施の形態においては、原料の芳香族炭化水素としてベンゼンが用いられたが、これに限られず、塩素化反応塔2で塩素化することの出来る全ての芳香族炭化水素が原料として用いられる。特に好ましい原料の芳香族炭化水素としては、ベンゼン以外に、トルエン、キシレン、エチルベンゼン等が例示され、製造目的物としては、p-ジクロロベンゼンの他に、モノクロロベンゼンおよびジクロロトルエン等が挙げられる。この場合、塩素化反応塔2の反応条件は、使用される原料の芳香族炭化水素に応じて適宜選択される。反応条件自体は公知である。また、洗浄塔4の洗浄液としては、原料の芳香族炭化水素が使用される。原料の芳香族炭化水素が洗浄液として用いられることにより、反応ガス中のより沸点の高い塩素化芳香族炭化水素類が効率よく抽出除去されると共に、この洗浄液が塩

素化反応塔に返送されることにより、塩素化反応の原料として再利用される。洗浄塔4の運転条件も、上記実施の形態の場合と同様の考え方が適用される。更に、断熱吸収塔6及びその他の装置、運転条件等も上記実施の形態と同様の考え方が適用されるので、その説明を省略する。

【0033】なお、本発明の塩酸の回収方法が組込まれるp-ジクロロベンゼン等の塩素化芳香族炭化水素の製造装置は、上記実施の形態の構成のものに限らず、現存する全ての装置に組込まれることができる。このような装置として、例えば、塩素化工程後生成する塩素化ベンゼン中のベンゼン及びモノクロロベンゼンを分離して塩素化工程に返送する工程を具備するもの、更には高次塩素化ベンゼンを分離してトランスクロロ化反応を行った後、塩素化工程に返送する工程を具備するもの等が挙げられる。

#### 【0034】

【実施例】実施例1～3、比較例1

実施例1～3として、図1に示す構成のp-ジクロロベンゼンの製造装置を用いて塩酸の回収を行った。

【0035】比較例として、塩素化反応塔2の塔頂から取出される反応ガスを洗浄塔4に送らず、直接断熱吸収式塩酸回収塔6に送る以外は実施例と同様にして、塩酸の回収を行った。

【0036】得られた結果を表1に示した。

#### 【0037】

【表1】

表 1

		比較例 1 ベンゼン 洗浄無し	実施例 1			実施例 2			実施例 3			
			ベンゼン			洗浄温度			洗浄圧力			
			洗浄有り			低下			上昇			
反応ガス (塩素化反応塔出口ガス)												
流量	kmol/H	8.45	←			←			←			
組成	Bz	mol%	0.387	←			←			←		
	MCH	mol%	0.930									
	n-DCB	mol%	0.005									
	p-DCB	mol%	0.321									
	o-DCB	mol%	0.079									
	TCB	mol%	0.001									
	HCl	mol%	98.278									
TOTAL		100.000										
ベンゼン供給量 m <sup>3</sup> /H		—	6			6			6			
洗浄温度 ℃		—	20			10			20			
洗浄圧力 kPa		—	1			1			10			
断熱吸収式塩酸回収塔入口ガス												
組成	H <sub>2</sub>	mol%	0.387	8.950			5.482			8.329		
	MCH	mol%	0.930	0.028			0.013			0.022		
	n-DCB	mol%	0.005	0.000			0.000			0.000		
	p-DCB	mol%	0.321	0.008			0.003			0.006		
	o-DCB	mol%	0.079	0.002			0.001			0.002		
	TCB	mol%	0.001	0.000			0.000			0.000		
	HCl	mol%	98.278	91.013			94.501			91.641		
TOTAL		100.000	100.000			100.000			100.000			
全有機化合物 ppm		51435	174786			110905			163592			
断熱吸収式塩酸回収塔排出ガスの蒸発液												
有機層比重		1.08	0.85			0.85			0.86			
塩酸層比重 (塩酸20wt%)		1.1	1.1			1.1			1.1			
濃度調整後の塩酸 (塩酸35wt%)												
全有機化合物 ppm		337	85			49			76			

【0038】実施例1においては、塩素化反応により得られる反応ガスを洗浄塔に送ってベンゼンによる洗浄操作を行った後、断熱吸収式塩酸回収塔で塩化水素の回収を行った。表1から明らかなように、断熱吸収式塩酸回収塔入口ガス(洗浄後の反応ガス)中の全有機化合物含有量は比較例1よりも多い。しかし、断熱吸収式塩酸回収塔排出ガスの凝縮液における塩酸層と、有機層との比重差は比較例の比重差よりも大きい。このため、実施例1の場合は塩酸層と有機層との液液分離が容易になり、塩酸回収塔に返送する塩酸層中に混入する有機化合物量が少なくなる。その結果、回収塔の塔底から取出して塩酸濃度調整工程で濃度を調整した後の塩酸に含まれる全有機化合物濃度は比較例1のそれよりも少なくなっている。

【0039】実施例2においては、洗浄塔の操作温度を実施例1よりも低下させた。表1から明らかなように、操作温度を下げるに、洗浄液であるベンゼンを含めて全

ての有機化合物の蒸気圧が減少するため、実施例1と比較し、洗浄後の反応ガス中の全有機化合物含有量が減少し、その結果濃度調整後の塩酸中の全有機化合物含有量も減少している。

【0040】実施例3においては、洗浄塔の操作圧力を実施例1よりも高めた。表1から明らかなように、操作圧力を高めると、有機化合物の分圧が減少するため、実施例1と比較し、洗浄後の反応ガス中の全有機化合物含有量が減少し、その結果濃度調整後の塩酸中の全有機化合物含有量も減少している。

【0041】比較例1においては、洗浄塔を経由して洗浄操作をすることなく、塩素化反応により得られる反応ガスを直接断熱吸収式塩酸回収塔に送り、塩酸の回収を行った。断熱吸収式塩酸回収塔入口ガス(反応ガス)中の全有機化合物含有量は実施例1～3と比較して少ない。しかし、断熱吸収式塩酸回収塔排出ガスの凝縮液の有機層と塩酸層との比重差が小さいため、液液分離効率

が悪い。また、高沸点の塩素化芳香族炭化水素が洗浄除去されないまま前記回収塔に供給され、それが該回収塔において気化せずに塩酸に混入される結果、濃度調整後の塩酸中の全有機化合物含有量は実施例1～3と比較して確かに多くなる。

## 【0042】

【発明の効果】本発明においては、原料の芳香族炭化水素を塩素化する際に生成する塩素化芳香族炭化水素等の有機化合物を含有する塩化水素ガスを、塩素化芳香族炭化水素よりも低沸点の芳香族炭化水素で洗浄し、塩化水素ガス中のより高沸点の塩素化芳香族炭化水素を沸点の低い芳香族炭化水素に置換することにより、断熱吸収式塩酸回収塔において有機化合物の凝縮を防止し、塔底から取出される粗塩酸中の有機化合物含有量を低減させる。更に、回収塔の塔頂から取出される排出ガスの凝縮液は、有機層と塩酸層とに分離されるが、前記有機層は塩素化芳香族炭化水素の含有量が少ないので比重が小さく、このため有機層と塩酸層との液液分離は容易で、互

に他層が混入することなく分離され、分離効率が高い。このようにして分離された有機層、及び塩酸層は互いの混入が避けられているので純度が高く、このためこれらは有効に再利用でき、その結果得られる製品塩酸の純度も高い。

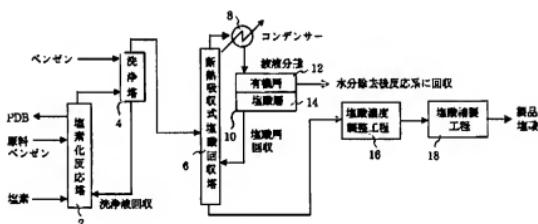
## 【図面の簡単な説明】

【図1】本発明の塩酸の回収方法を組んだ塩素化ベンゼンの製造装置の一例を示すフロー図である。

## 【符号の説明】

2	塩素化反応塔
4	洗浄塔
6	断熱吸収式塩酸回収塔
8	コンデンサー
10	液液分離器
12	有機層
14	塩酸層
16	塩酸濃度調整工程
18	塩酸精製工程

【図1】



フロントページの続き

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**(57) Abstract**

**Technical problem** The recovery method of the chloride which reduces the organic compound content in the chloride which carries out a byproduction in the chlorinating reaction of aromatic hydrocarbon, such as benzene, is provided.

**Means for Solution**Chlorinate benzene with the chlorinating reaction tower 2, and are in charge of manufacturing p-dichlorobenzene, Absorption removal of the organic compound of a high boiling point is carried out to benzene rather than benzene which contacts with benzene reactant gas containing the hydrogen chloride gas emitted in said chlorinating reaction in the washing tower 4, and is contained in said reactant gas, Subsequently, send reactant gas after absorption removal to the heat insulation absorption type chloride reclaiming tower 6, and raw salt acid is obtained from a bottom of the reclaiming tower 6, and emission gas is obtained from the overhead of the reclaiming tower 6.

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**Claim(s)**

**Claim 1**In manufacturing chlorinated aromatic hydrocarbon by a chlorinating reaction of aromatic hydrocarbon, Absorption removal of the chlorinated aromatic hydrocarbon of a high boiling point is carried out to this aromatic hydrocarbon rather than this aromatic hydrocarbon that contacts reactant gas containing the hydrogen chloride gas emitted in said chlorinating reaction to aromatic hydrocarbon of a raw material, and is contained in said reactant gas, Subsequently, a recovery method of chloride which send reactant gas after absorption removal to a heat insulation absorption type chloride reclaiming tower, and raw salt acid is obtained from a bottom, and is characterized by extracting emission gas from the overhead.

**Claim 2**A recovery method of the chloride according to claim 1 which is made to condense emission gas, carries out liquid-liquid separation to an organic layer and a chloride layer which use aromatic hydrocarbon of a raw material as the main ingredients, and is reused to a chlorinating reaction after drying said organic layer.

**Claim 3**A recovery method of the chloride according to claim 1 which makes emission gas

condense, carries out liquid-liquid separation to an organic layer and a chloride layer which use aromatic hydrocarbon of a raw material as the main ingredients, and returns said chloride layer to a heat insulation absorption type chloride reclaiming tower.

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### **Detailed Description of the Invention**

**0001**

**Field of the Invention** This invention relates to the method of collecting chlorides from the hydrogen chloride gas which carries out a byproduction in the chlorinating reaction of aromatic hydrocarbon, such as benzene and toluene.

**0002**

**Description of the Prior Art** The dichlorobenzene (DCB) produced by chlorinating benzene is an important compound industrially. There are three isomers of alt.dichlorobenzene (o-DCB), meta-dichlorobenzene (m-DCB), and PARAJI chlorobenzene (p-DCB) in dichlorobenzene. Among these three isomers, PDCB has most demand, and is used for an insecticide etc., and attracts attention as a raw material of the polyphenylene sulfide which is engineering plastics.

**0003** Conventionally, dichlorobenzene is manufactured by chlorinating benzene (BZ) or chlorobenzene (CB) using the Friedel craft type catalysts, such as ferric chloride.

**0004** In order to raise the selectivity of PARAJI chlorobenzene at the time of manufacture, the method of using together the inorganic matter or the organic compound, and ferric chloride of sulfur and a selenium series as a catalyst is also proposed.

**0005** In the chlorinating reaction of benzene or monochlorobenzene, the art which raises the selectivity of PARAJI chlorobenzene is also proposed by using zeolite as a catalyst (JP,57-77631,A, JP,59-163329,A).

The art which solves the problem which conventional technology has is also indicated by using activated alumina as a catalyst (JP,1-93550,A).

**0006** In these manufacturing methods, although benzene is chlorinated by each under existence of a catalyst in the gaseous phase or the liquid phase, in this chlorinating reaction, the byproduction of the hydrogen chloride is carried out and this is taken out outside as byproduction hydrogen chloride gas. In the byproduction hydrogen chloride gas taken out by said exterior, Since various chlorinated benzene, such as benzene which is a raw material of a chlorinating reaction and chlorobenzene which is resultants, dichlorobenzene, and trichlorobenzene (TCB), contains according to the steam pressure at least, Said byproduction hydrogen chloride gas is cooled beforehand, benzene and chlorinated benzene are condensed, and collecting and using is performed.

**0007** However, the recovery by said condensation is not perfect and the quantity equivalent to the steam pressure of each organic compound, such as benzene at cooling temperature, still remains in byproduction hydrogen chloride gas. For this reason, this byproduction hydrogen chloride gas is sent to a chloride reclaiming tower, and these chlorinated benzene is contained in the chloride produced by contacting in water here.

**0008** Benzene and chlorinated benzene are contained in the emission gas taken out from the overhead side of a chloride reclaiming tower in addition to water and hydrogen chloride.

These are condensed by being cooled and layer separation is carried out to the organic layer and chloride layer which use benzene as the main ingredients.

Usually, liquid-liquid separation of these organic layers and chloride layers that carried out layer separation is carried out. However, since said organic layer contains chlorinated benzene, its specific gravity is close to chloride. For this reason, the liquid-liquid separation of a chloride layer and an organic layer is difficult, and, as a result, it comes to bring trouble to a subsequent chloride purification process, and collecting said organic layers and using as manufacturing raw materials again also has problems, such as becoming difficult.

**0009**

**Problem(s) to be Solved by the Invention** In order to solve the above-mentioned problem, as a result of this invention persons' examining many things, when contacting the byproduction hydrogen chloride gas emitted in the chlorinating reaction of benzene with benzene, If it sends to a heat insulation absorption type reclaiming tower and raw salt acid is manufactured after making

the chlorinated benzene contained in byproduct hydrogen chloride gas replace by benzene, may decrease substantially the organic matter content in the raw salt acid taken out from the bottom of a reclaiming tower, and. Although the emission gas taken out from the overhead is condensed by cooling and it separates into a chloride layer and an organic layer, Specific gravity of the organic layer was smaller than the chloride layer enough in order to use benzene as the main ingredients, for this reason, simply, the above-mentioned two-layer ones could carry out liquid-liquid separation, and learning of the ability of each class produced by doing in this way to be used effectively, respectively was carried out. Learning of a described method not being restricted to benzene but being able to apply it to various kinds of general aromatic compounds was carried out. This invention comes to be completed based on the above-mentioned knowledge.

**0010**Therefore, there is a place made into the purpose of this invention in providing the recovery method of the chloride which solves the conventional problem.

**0011**

**Means for Solving the Problem**This invention for attaining the above-mentioned purpose is indicated below.

**00121**In manufacturing chlorinated aromatic hydrocarbon by a chlorinating reaction of aromatic hydrocarbon, Absorption removal of the chlorinated aromatic hydrocarbon of a high boiling point is carried out to this aromatic hydrocarbon rather than this aromatic hydrocarbon that contacts reactant gas containing the hydrogen chloride gas emitted in said chlorinating reaction to aromatic hydrocarbon of a raw material, and is contained in said reactant gas, Subsequently, a recovery method of chloride which send reactant gas after absorption removal to a heat insulation absorption type chloride reclaiming tower, and raw salt acid is obtained from a bottom, and is characterized by extracting emission gas from the overhead.

**00132**Emission gas is made to condense, liquid-liquid separation is carried out to an organic layer and a chloride layer which use aromatic hydrocarbon of a raw material as the main ingredients, and it reuses to a chlorinating reaction after drying said organic layer. A recovery method of chloride given in **1**.

**00143**Emission gas is made to condense, liquid-liquid separation is carried out to an organic layer and a chloride layer which use aromatic hydrocarbon of a raw material as the main ingredients, and said chloride layer is returned to a heat insulation absorption type chloride reclaiming tower. A recovery method of chloride given in **1**.

**0015**Hereafter, with reference to drawings, this invention is explained in detail.

**0016**

**Embodiment of the Invention**Drawing 1 is a flow chart showing an example of the manufacturing installation of the p-dichlorobenzene incorporating the recovery method of the chloride of this invention.

**0017**Two are a chlorinating reaction tower among drawing 1, and the inside is filled up with the catalyst. As a catalyst, the Friedel craft type catalysts, such as a solid acid catalyst of publicly known activated alumina, silica alumina, crystalline aluminosilicate, etc., ferric chloride, an aluminium chloride, etc. are illustrated. Benzene, chlorine, etc. which are aromatic hydrocarbon of a raw material are supplied to said chlorinating reaction tower 2, these react to it within the chlorinating reaction tower 2, and the chlorinated benzene which uses p-dichlorobenzene as the main ingredients is taken out as a resultant. This reaction itself is publicly known.

**0018**In said chlorinating reaction, although reactant gas is emitted, hydrogen chloride gas is made this reactant gas with the main ingredients, and chlorinated benzene, such as raw material benzene and monochlorobenzene, o-, m-, p-dichlorobenzene, and trichlorobenzene, is contained as other ingredients.

**0019**This reactant gas is sent to the bottom side of the washing tower 4, after it is taken out from the overhead of the chlorinating reaction tower 2 and necessity carries out condensation removal of said some of chlorinated benzene through a heat exchanger (un-illustrating) here.

**0020**While the penetrant remover benzene supplied from the overhead side in said washing tower 4 flows down the inside of the washing tower 4, Gas-liquid contact is repeated in the state of the reactant gas which is supplied from the bottom side and goes up the inside of a washing tower, and a counterflow, Extraction removal is carried out with the benzene down which the organic compound (chlorinated benzene, such as CB, DCB, TCB, tetrachlorobenzene, and hexachlorobenzene) of a high boiling point flows rather than the benzene in reactant gas by this.

**0021** Subsequently to the bottom side of the chlorinating reaction tower 2 the benzene solution (penetrant remover) which flowed down the inside of the washing tower 4 while extracting the organic compound of the high boiling point rather than benzene is returned, and is reused as a raw material of a chlorinating reaction.

**0022** The washing tower 4 can use the device used as common gas absorbers, such as a packed column, a tray tower, a wetted wall column, a spray tower, and a bubbling tower. Pressure loss of a packed column is comparatively small, and since gas absorption efficiency is high, it is **among these** desirable. As an operating condition of the liquid/gas mass flow of a packed column, below flooding velocity, especially 50% of flooding velocity order are preferred.

**0023** The yield of hydrogen chloride gas is large, and when the tower diameter of a washing tower becomes large, use of a tray tower is preferred.

**0024** Since penetrant remover benzene is carried in by entrainment into reactant gas, a spray tower can be used if cautious of this point.

**0025** Since its benzene content in the reactant gas after washing decreases so that the operating temperature of the washing tower 4 is generally low temperature, its low-temperature one is preferred. However, since it is necessary to operate it above the coagulating point (5\*\*) of penetrant remover benzene, 5-30 \*\* is preferred and 7-10 \*\* is especially desirable.

**0026** The high voltage of the operating pressure power of the washing tower 4 is more preferred. The steam pressure of penetrant remover benzene becomes low, so that it is high voltage, and as a result, the benzene content in the reactant gas after washing decreases. However, since high pressure installation is expensive, it is preferred to operate it by the pressure of 1 or less MPa. If decompression is used, since the partial pressure of organic compounds, such as benzene and chlorinated benzene, will become large and the benzene in the reactant gas after washing and the content of an organic compound will increase as a result, it is not desirable. Therefore, the operating pressure power of a washing tower has ordinary pressure - preferred 1MPa.

**0027** The inside of the washing tower 4 is gone up, and subsequently to the heat insulation absorption type chloride reclaiming tower 6 the reactant gas of chlorinated benzene with which all were almost removed is sent, hydrogen chloride in reactant gas is absorbed by the water which flows down the inside of a tower here, and it serves as raw salt acid, and is taken out from the bottom side of the reclaiming tower 6.

**0028** Structurally, the heat insulation absorption type chloride reclaiming tower 6 is a thing of the same structure mostly with said washing tower 4. Heat insulation absorption of the hydrogen chloride in reactant gas is functionally carried out in the reclaiming tower 6 at water. As a result of barring condensation of the chlorinated benzene which exists in the benzene which water is evaporated by the rise in heat based on the big heat of solution generated in that case, and is contained in reactant gas, or a minute amount, it is avoided that those organic matters mix into raw salt acid.

**0029** The raw salt acid taken out from the bottom side of said heat insulation absorption type chloride reclaiming tower 6 passes the chloride purification process 18 by the hydrochloric-acid-concentration adjusting process 16, activated carbon treatment, etc. one by one after that, and is taken out as product chloride.

**0030** On the other hand, emission gas is taken out from the overhead side of the heat insulation absorption type chloride reclaiming tower 6. The great portion of hydrogen chloride gas in reactant gas is the gas by which absorption removal was carried out, and this emission gas mainly consists of the steam and the slight hydrogen chloride gas which occupy most, and benzene gas, when water and reactant gas carry out countercurrent contact in the reclaiming tower 6.

**0031** It is cooled when passing the capacitor 8 first, and said emission gas becomes a condensate, is sent to the liquid-liquid separation machine 10, and is divided into the organic layer 12 and the chloride layer 14 here.

**0032** Said separated chloride layer is returned after that to the pars intermedia of the overhead of the heat insulation absorption type chloride reclaiming tower 6, and a bottom. Said separated organic layer 12 is returned and reused by the chlorinating reaction tower 2 after dehydrating treatment is made using solid dehydrators, such as distillation, silica gel, a molecular sieve, anhydrous sodium sulfate, etc. In the above-mentioned embodiment, although benzene was used as aromatic hydrocarbon of a raw material, it is not restricted to this but all the aromatic hydrocarbon which can be chlorinated with the chlorinating reaction tower 2 is used as a raw

material. Especially, as aromatic hydrocarbon of a desirable raw material, in addition to benzene, toluene, xylene, ethylbenzene, etc. are illustrated and monochlorobenzene, dichlorotoluene, etc. other than p-dichlorobenzene are mentioned as a manufacture object. In this case, the reaction condition of the chlorinating reaction tower 2 is suitably chosen according to aromatic hydrocarbon of the raw material used. The reaction condition itself is publicly known. Aromatic hydrocarbon of a raw material is used as a penetrant remover of the washing tower 4. By using aromatic hydrocarbon of a raw material as a penetrant remover, extraction removal of the chlorinated aromatic hydrocarbon in which the boiling point is higher than that in reactant gas is carried out efficiently, and it is reused as a raw material of a chlorinating reaction by returning this penetrant remover to a chlorinating reaction tower. The view as the case of the above-mentioned embodiment that the operating condition of the washing tower 4 is also the same is applied. Since the view as the above-mentioned embodiment that the heat insulation absorption tower 6 and other devices, an operating condition, etc. are the same is applied, the explanation is omitted.

**0033**The manufacturing installation of chlorinated aromatic hydrocarbon, such as p-dichlorobenzene into which the recovery method of the chloride of this invention is built, cannot be restricted to the thing of the composition of the above-mentioned embodiment, but can be included in all the existing devices. The thing possessing the process which separates the benzene and monochlorobenzene in the chlorinated benzene generated after a chlorination process as such a device, for example, and is returned to a chlorination process, After separating high order chlorinated benzene and performing a transformer chloro-ized reaction, the thing possessing the process returned to a chlorination process, etc. are mentioned.

**0034**

**Example**Chlorides were collected using the manufacturing installation of the p-dichlorobenzene of composition of being shown in drawing 1 as Examples 1-3 and comparative example 1 Examples 1-3.

**0035**Chlorides were collected like the example except not sending the reactant gas taken out from the overhead of the chlorinating reaction tower 2 to the washing tower 4 as a comparative example, but sending to the direct heat insulation absorption type chloride reclaiming tower 6.

**0036**The obtained result was shown in Table 1.

**0037**

**Table 1**

**0038** In Example 1, after sending the reactant gas obtained by a chlorinating reaction to the washing tower and performing washing operation by benzene, hydrogen chloride was collected in the heat insulation absorption type chloride reclaiming tower. There is more all the organic compound content in heat insulation absorption type chloride reclaiming tower entrance gas (reactant gas after washing) than the comparative example 1 so that clearly from Table 1. However, the specific gravity difference of the chloride layer in the condensate of heat insulation absorption type chloride reclaiming tower emission gas and an organic layer is larger than the specific gravity difference of a comparative example. For this reason, in the case of Example 1, the liquid-liquid separation of a chloride layer and an organic layer becomes easy, and the amount of organic compounds mixed into the chloride layer returned to a chloride reclaiming tower decreases. As a result, the total organic compound concentration contained in the chloride after taking out from the bottom of a reclaiming tower and adjusting concentration by a hydrochloric-acid-concentration adjusting process has become less than that of the comparative example 1.

**0039** In Example 2, the operating temperature of the washing tower was reduced rather than Example 1. Since the steam pressure of all the organic compounds including the benzene which is a penetrant remover will decrease if operating temperature is lowered so that clearly from Table 1,

as compared with Example 1, all the organic compound content in the reactant gas after washing decreases, and, as a result, all the organic compound content in the chloride after concentration adjustment is also decreasing.

**0040** In Example 3, the operating pressure power of the washing tower was heightened rather than Example 1. Since the partial pressure of an organic compound will decrease if operating pressure power is heightened so that clearly from Table 1, as compared with Example 1, all the organic compound content in the reactant gas after washing decreases, and, as a result, all the organic compound content in the chloride after concentration adjustment is also decreasing.

**0041** In the comparative example 1, without carrying out washing operation via a washing tower, the reactant gas obtained by a chlorinating reaction was sent to the direct heat insulation absorption type chloride reclaiming tower, and chlorides were collected. There is little all the organic compound content in heat insulation absorption type chloride reclaiming tower entrance gas (reactant gas) as compared with Examples 1-3. However, since the specific gravity difference of the organic layer of the condensate of heat insulation absorption type chloride reclaiming tower emission gas and a chloride layer is small, liquid-liquid separation efficiency is bad. While washing removal of the chlorinated aromatic hydrocarbon of a high boiling point has not been carried out, said reclaiming tower is supplied, and as a result of being mixed in chloride, without it evaporating in this reclaiming tower, all the organic compound content in the chloride after concentration adjustment increases far as compared with Examples 1-3.

#### **0042**

**Effect of the Invention** The hydrogen chloride gas containing organic compounds, such as chlorinated aromatic hydrocarbon generated in this invention when chlorinating aromatic hydrocarbon of a raw material, Low-boiling-point aromatic hydrocarbon washes rather than chlorinated aromatic hydrocarbon, and chlorinated aromatic hydrocarbon of a high boiling point is replaced by low aromatic hydrocarbon of the boiling point from that in hydrogen chloride gas. Therefore, condensation of an organic compound is prevented in a heat insulation absorption type chloride reclaiming tower, and the organic compound content in the raw salt acid taken out from a bottom is reduced.

Although the condensate of the emission gas taken out from the overhead of a reclaiming tower is divided into an organic layer and a chloride layer, since said organic layer has little content of chlorinated aromatic hydrocarbon, its specific gravity is small, it is easy, and it dissociates without other layers mixing mutually, and separation efficiency is high **the liquid-liquid separation of an organic layer and a chloride layer** for this reason. Thus, since mutual mixing is avoided, the separated organic layer and a chloride layer have high purity, and as for these, the purity of the product chloride which can reuse effectively and is obtained as a result is also high for this reason.

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#### **Brief Description of the Drawings**

**Drawing 1** It is a flow chart showing an example of the manufacturing installation of the chlorinated benzene incorporating the recovery method of the chloride of this invention.

#### **Description of Notations**

- 2 Chlorinating reaction tower
- 4 Washing tower
- 6 Heat insulation absorption type chloride reclaiming tower
- 8 Capacitor
- 10 Liquid-liquid separation machine
- 12 Organic layer
- 14 Chloride layer
- 16 Hydrochloric-acid-concentration adjusting process
- 18 Chloride purification process

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#### **Drawing 1**

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